01 Solid State

Introduction

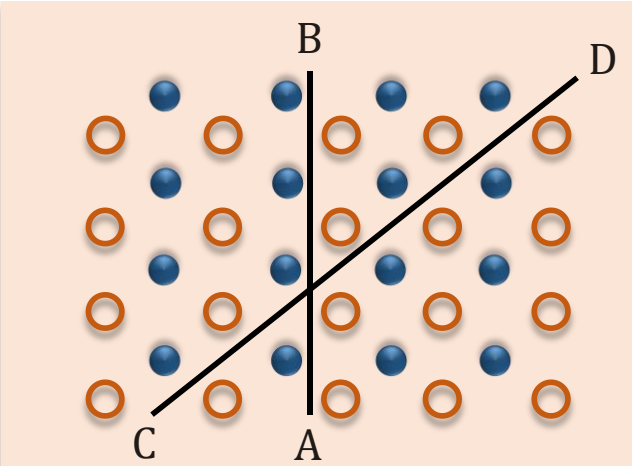
The solids are characterised by incompressibility, rigidity and mechanical strength. The molecules, atoms or ions in solids are closely packed. It means that they are held together by strong forces and can not move randomly. Thus solids have definite volume, shape, slow diffusion, low vapour pressure and possess the unique property of being rigid. Such solids are known as **true solids** like NaCl, KCl, Sugar, Ag, Cu etc. On the other hand the solid which loses shape on long standing, flows under its own weight and easily gets distorted by even mild distortion forces are called **pseudo solids** such as glass, pitch etc.

Some solids such as NaCl, Sugar, Sulphur etc. have not only rigidity and incompressibility properties but also have typical geometrical forms. These solids are called as **crystalline solids**. In such solids there is a definite arrangement of particles (atoms, ions or molecules) throughout the entire three dimensional network of a crystal in the long-range order. This three dimensional arrangement is called **crystal lattice or space lattice**. Other solids such as glass, rubber, plastics etc. have rigidity and incompressibility to a certain extent but they do not have a definite geometrical form or does not have long range order and are known as **amorphous solids**.

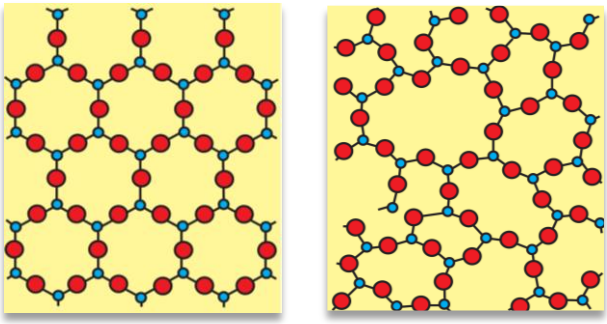
Distinction between Crystalline and Amorphous Solids

Property	Crystalline solids	Amorphous solids
Shape	Definite characteristic geometrical shape	Irregular shape
Melting point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
Heat of fusion	They have a definite and characteristic heat of fusion	They do not have definite heat of fusion
Anisotropic nature	Anisotropic in nature (direction dependent)	Isotropic in nature (direction independent)
Nature	True solids	Pseudo solids or super cooled liquids
Arrangement of particles	Long range order	Only short range order
Examples	NaCl, Metals, Diamond	Rubber, Plastics

★ Golden Key Points ★



Anisotropy in crystals is due to different arrangement of particles along different directions



(a) (b)

Two dimensional structure of (a) quartz and (b) quartz glass

Table (a): Classification of crystalline solids

S. No.	Types of Solid	Constituent Particles	Bonding/ Attractive Forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
1	Molecular Solids (i) None Polar	Molecules	Dispersion or London forces	Ar, CCl_4, H_2, I_2CO_2	Soft	Insulator	Very low
	(ii) Polar		Dipole-dipole interactions	HCl, SO_2	Soft	Insulator	Low
	(iii) Hydrogen bonded		Hydrogen bonding	H_2O (ice)	Hard	Insulator	Low
2	Ionic solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF_2	Hard but brittle	Insulator in solid state but conductors in molten and in aquesous solution	High
3	Metallic solids	Positive metal ions in a sea of delocalised e^-	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid and in molten state	Fairly high
4	Covalent or network solids	Atoms	Covalent bonds	SiO_2, SiC, AlN C(diamond) C(graphite)	Hard Soft	Insulators Conductor	Very high

Illustration 1:

Assertion: Crystalline solids are anisotropic.

Reason: The constituent particles are very closely packed.

(1) A (2) B (3) C (4) D

Ans. (2)

Illustration 2:

Classify the following as amorphous or crystalline solids:

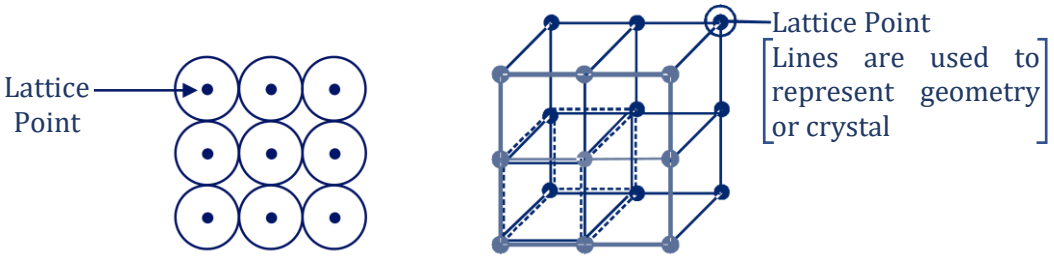
(a) Polyurethane (b) Naphthalene (c) Benzoic acid (d) Teflon
(e) Potassium nitrate (f) Cellophane (g) Polyvinyl chloride (h) Fiber glass
(i) Copper

Solution:

(a) Amorphous (b) Crystalline (c) Crystalline (d) Amorphous
(e) Crystalline (f) Amorphous (g) Amorphous (h) Amorphous
(i) Crystalline

Space Lattice/Crystalline Lattice/3–D Lattice

- Space lattice is a regular arrangement of lattice points (atoms or ions or molecules) showing how the particles are arranged at different sites in 3D–view.



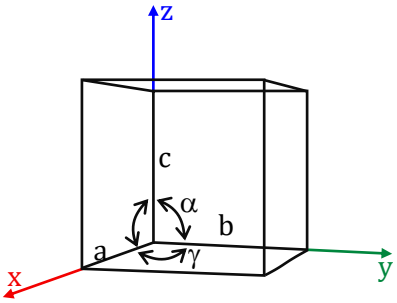
- The three dimensional distribution of component particles in a crystal can be found by X-ray diffraction of different faces of the crystal.
- On the basis of the shape and geometry, the crystals have been divided into seven systems. These seven systems with their characteristics of Interfacial angles and intercepts with examples of each are given in the following table (b).

  These crystal systems differ in length of unit cell edges (a, b and c) and the angles between the unit cell edges.

  In cubic and trigonal (rhombohedral) systems, the three unit edges are of equal lengths but for the rest five systems it is not so. The interfacial angles are all 90° in the cubic, tetragonal and orthorhombic systems but it is not so for the rest of the four systems.

Unit Cell (U.C.)

Unit cell of the crystalline substance is defined as the smallest repeating portion which shows the complete geometry of the crystalline substance like brick in a wall. A unit cell is the smallest portion of the whole crystal. A unit cell is characterized by the edge lengths a, b and c along the three axes of the unit cell and the angles α, b β and γ between the pair of edges bc, ca and ab respectively.



S. No.	System	Name of Lengths	Edge Angles	Bravais Lattices	Examples
1.	Cubic	a = b = c	$\alpha = \beta = \gamma = 90^\circ$	Primitive, Face-centred, Body centred = 3	NaCl, Zinc blende, Cu
2.	Tetragonal	a = b ≠ c	$\alpha = \beta = \gamma = 90^\circ$	Primitive, Body centred = 2	White tin, SnO_2, TiO_2, $CaSO_4$
3.	Orthorhombic Or Rhombic	a ≠ b ≠ c	$\alpha = \beta = \gamma = 90^\circ$	Primitive, Face-centred, Body centred, End centred = 4	Rhombic Sulphur, KNO_3, $BaSO_4$ Match Box.
4.	Rhombohedral or Trigonal	a = b = c	$\alpha = \beta = \gamma \neq 90^\circ$	Primitive = 1	Calcite ($CaCO_3$), HgS (cinnabar)
5.	Hexagonal	a = b ≠ c	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Primitive = 1	Graphite, ZnO, CdS
6.	Monoclinic	a ≠ b ≠ c	$\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$	Primitive, End centred = 2	Monoclinic Sulphur, $Na_2SO_4.10H_2O$
7.	Triclinic	a ≠ b ≠ c	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Primitive = 1	$K_2Cr_2O_7$, $CuSO_4.5H_2O$, H_3BO_3
				Total = 14	

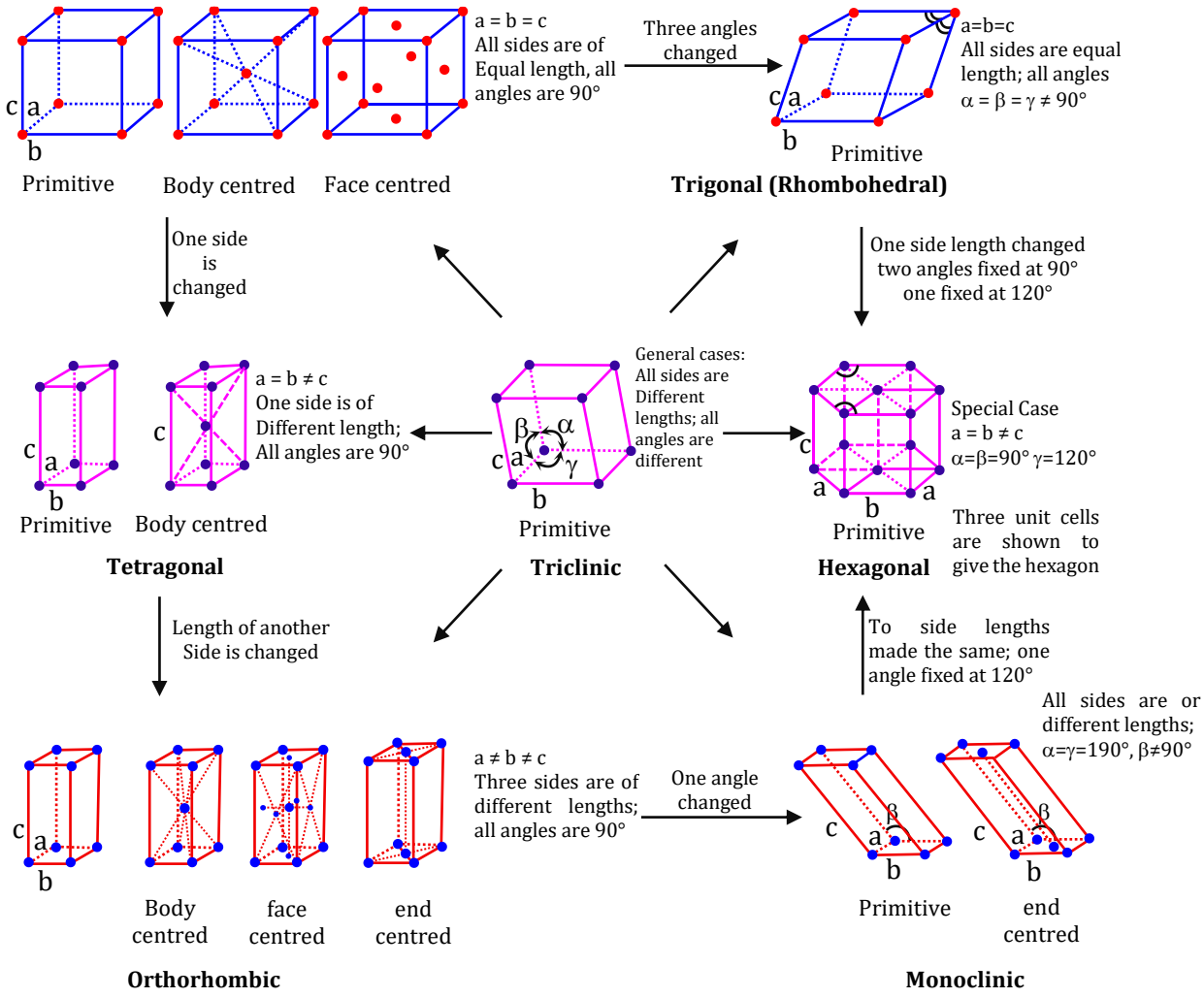

a = b = c
All sides are of Equal length, all angles are 90°
Primitive
Body centred
Face centred
Three angles changed
a=b=c
All sides are equal length; all angles
α = β = γ ≠ 90°
Primitive
Trigonal (Rhombohedral)
One side is changed
One side length changed two angles fixed at 90° one fixed at 120°
a = b ≠ c
One side is of Different length; All angles are 90°
Primitive
Body centred
Tetragonal
General cases: All sides are Different lengths; all angles are different
Primitive
Triclinic
Special Case
a = b ≠ c
α=β=90° γ=120°
Primitive
Hexagonal
Three unit cells are shown to give the hexagon
Length of another Side is changed
To side lengths made the same; one angle fixed at 120°
All sides are or different lengths; α=γ=190°, β≠90°
a ≠ b ≠ c
Three sides are of different lengths; all angles are 90°
One angle changed
Body centred
face centred
end centred
Orthorhombic
Primitive
end centred
Monoclinic

Illustration 3:

For a crystal, unit cell parameters are as follows a = b = 4.2 Å, c = 5.1 Å Crystal system may be

(1) Tetragonal (2) Orthorhombic (3) Hexagonal (4) Either 1 or 3

Ans. (4)

Illustration 4:

Which of the following is a non-crystalline solid ?

(1) Diamond (2) NaCl (3) CaF_2 (4) Rubber

Ans. (4)

Co-ordination Number

The number of nearest neighbouring particles around a specific particle in a given crystalline substance is called as co-ordination number of that crystalline substance.

Packing Efficiency or Packing fraction (P.E.)

"Packing efficiency is defined as the ratio of volume occupied by the atoms to the total volume of the crystalline substance"

$$\text{P.E.} = \frac{\text{Volume occupied by atoms present in a crystal}}{\text{Volume of crystal}}$$

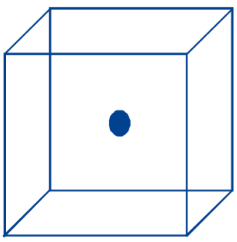
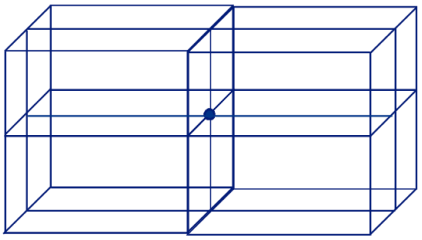
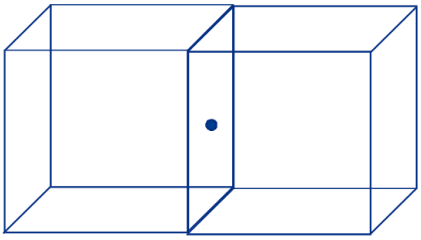
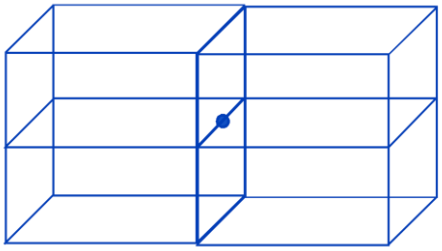
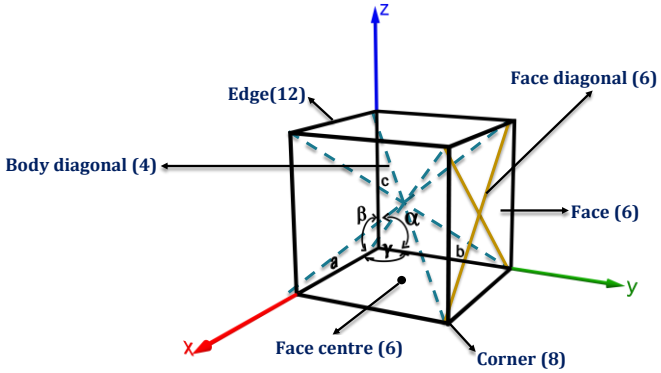
$$\text{P.E.} = \frac{\text{Volume occupied by atoms present in a unit cell}}{\text{Volume of unit cell}} \text{ or P.E.} = \frac{z\times(4/3)\pi r^3}{V}$$

or

Where z = number of atoms present in unit cell / Number of formula units for ionic crystals.

Golden Key Points

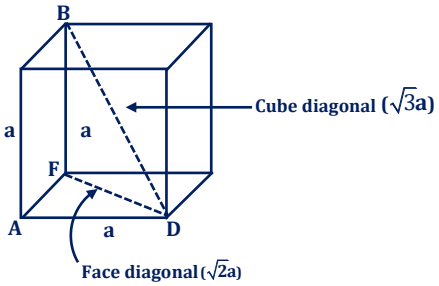
- **In a cube**
  1. Number of corners = 8
  2. Number of faces = 6
  3. Number of edges = 12
  4. Number of body centre = 1
  5. Number of body diagonals = 4
  6. Number of face diagonals = 12

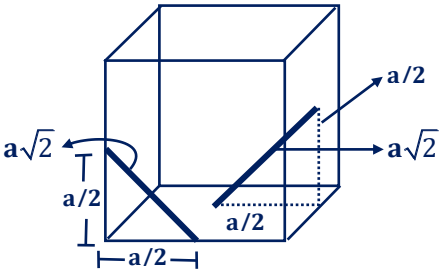






Contribution of an atom at different lattice points of cube:

- A corner of a cube is common in 8 cubes. So $\frac{1}{8}$ th part of an atom is present at this corner of cube.
- A face of a cube is common in 2 cubes. So $\frac{1}{2}$ th part of an atom is present at the face of a cube.
- An edge of a cube is common in four cubes, so $\frac{1}{4}$ th part of the atom is present at the edge of a cube
- A cube centre is not common in any another cube, so one complete atom is present at the cube centre.

Length of Face Diagonal and Cube Diagonal





Distance between 2 adjacent face centres = $\frac{a}{\sqrt{2}} = \frac{a\sqrt{2}}{2}$

Distance between 2 adjacent edge centres = $\frac{a}{\sqrt{2}} = \frac{a\sqrt{2}}{2}$

Consider the triangle AFD (with the help of pyathogorous theorem)

$FD = \sqrt{AF^2 + AD^2} = \sqrt{a^2 + a^2} = \sqrt{2}a$ (length of face diagonal.)

Consider the triangle BFD (with the help of pyathogorous theorem)

$BD = \sqrt{BF^2 + FD^2} = \sqrt{a^2 + (\sqrt{2}a)^2} = \sqrt{3}a$ (length of cube diagonal)

Density of The Crystal (d OR ρ)

If the length of edge of the unit cell is known we can calculate the density of the crystal as follow:

Let length of edge of the unit cell be 'a' cm.

∴ Volume of the cubic unit cell = V $cm^3 = a^3$ cm^3

Density of the unit cell = $\frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$

Let mass of N particles present in a lattice = m g

mass of 1 particle present in a lattice = $\frac{m}{N}$ g

mass of z particles present in lattice = $\frac{z \times m}{N}$ g

$$\boxed{d = \frac{z \times m}{N \times a^3}}$$

where z = number of particles or number of formula units (for ionic crystals) in the 1 unit cell

m = mass of lattice in g

d = density (g/cm^3)

a = edge length in cm

if m = M (molar mass)

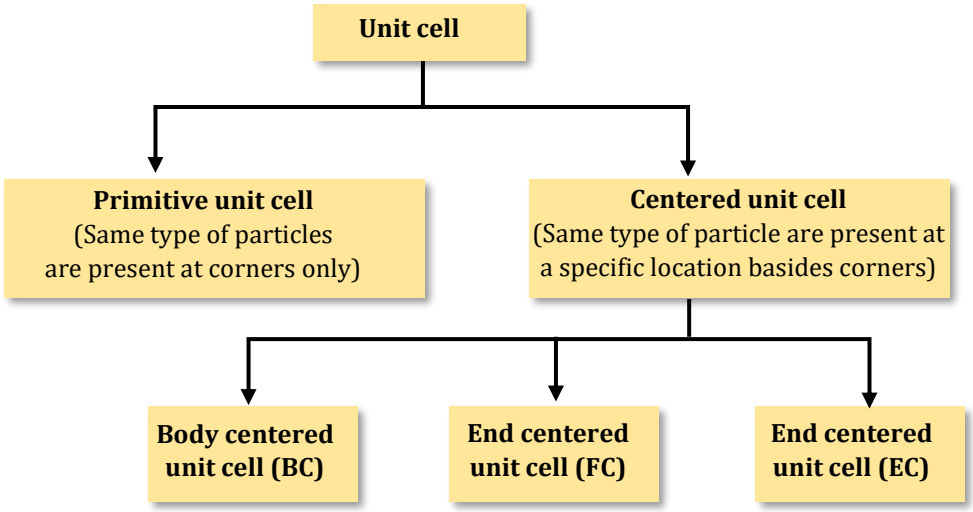
then $N = N_A$

$$d = \frac{z \times M}{N_A \times a^3}$$

Golden Key Points

- If number of particles in a lattice = N
  number of SC unit cell = N
  number of bcc unit cell = $\frac{N}{2}$
  number of fcc unit cell = $\frac{N}{4}$
- For calculations use $N_A = 6 \times 10^{23}$
- 1 pm = 10^{-12} m = 10^{-10} cm
- 1 Å = 10^{-10} m = 10^{-8} cm

Classification of a Unit Cell (As per Bravais)


Unit cell
Primitive unit cell
(Same type of particles are present at corners only)
Centered unit cell
(Same type of particle are present at a specific location basides corners)
Body centered unit cell (BC)
End centered unit cell (FC)
End centered unit cell (EC)

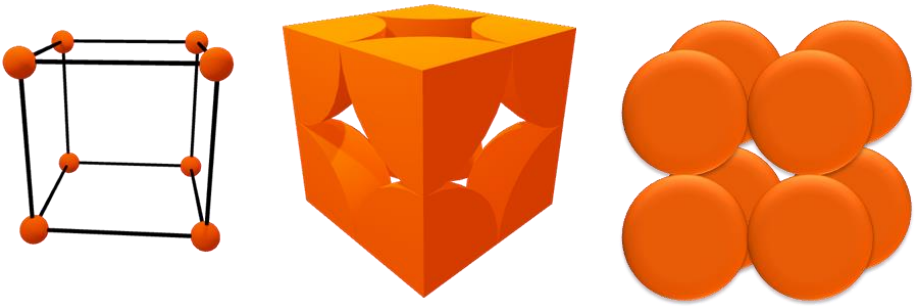
- In end centered UC same type of particles are present at corners and any two opposite face centres.
- End centered type of Bravais lattice is present only in orthorhombic and monoclinic type of unit cell.

Types of Cubic Unit Cell

On the basis of location of lattice points in the unit cell, unit cells can be divided in the following classes:

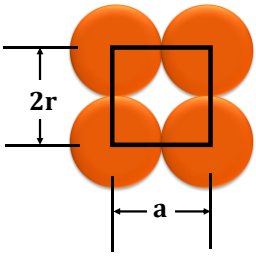
(A) Simple/Primitive/Basic Cubic Unit Cell

A unit cell having lattice point only at corners is called primitive or simple unit cell. i.e. in this case there is one atom at each of the eight corners of the unit cell considering an atom at one corner as the centre, it will be found that this atom is surrounded by six equidistant neighbours (atoms) and thus the co-ordination number will be six. If 'a' is the side of the unit cell, then the distance between the nearest neighbours shall be equal to 'a'.



(a) Relationship between edge length 'a' and atomic radius 'r':

a = 2r i.e. $\boxed{r = \frac{a}{2}}$



(One face of SC)

(b) Number of atoms present in unit cell (z): In this case one atom lies at the each corner. Hence simple cubic unit cell contains a total of $\frac{1}{8}\times 8$ = 1 atom / unit cell.

(c) Packing efficiency (P. E.):

$$\text{P.E.} = \frac{\text{Volume occupied by atoms present in unit cell}}{\text{Volume of unit cell}} = \frac{z\times\frac{4}{3}\pi r^3}{V} \quad \left[\because \text{Volume of atom} = \frac{4}{3}\pi r^3\right]$$

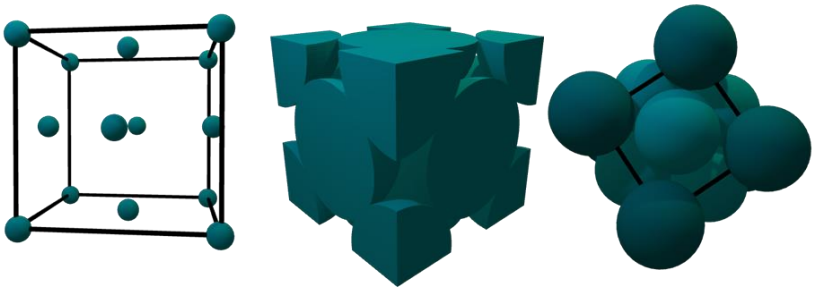
$$\text{For SC: P.E.} = \frac{1\times\frac{4}{3}\times\pi\times\left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6} = 0.524 \text{ or } 52.4\% \quad [\because r = \frac{a}{2} \text{ and } V = a^3, z = 1]$$

In SC, 52.4% of total volume is occupied by atoms

% void space = 47.6

(B) Face Centred Cubic Unit Cell (FCC)

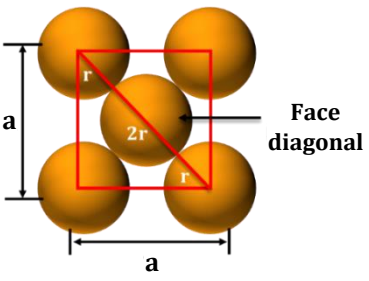
A unit cell having lattice point at every face centre in addition to the lattice point at every corner called as face centred unit cell. i.e. in this case there are eight atoms at the eight corners of the unit cell and six atoms at the centre of six faces. The co-ordination number will be 12 and the distance between the two nearest atoms will be $\frac{a\sqrt{2}}{2}$



(a) Relationship between edge length 'a' and atomic radius 'r':

In FCC, along the face diagonal all atoms touches each other and the length of face diagonal is $\sqrt{2}$ a.

So $4r = \sqrt{2}\,a$ i.e.$r = \frac{\sqrt{2}a}{4} = \frac{a}{2\sqrt{2}}$ $\boxed{r = \frac{a}{2\sqrt{2}}}$



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(b) Number of atoms per unit cell (z):

$z = \left(\frac{1}{8}\times 8\right) + \left(6\times\frac{1}{2}\right)$ = 1 + 3 = 4 atoms/unit cell

Corners faces

In this case one atom lies at the each corner of the cube and one atom lies at the centre of each face of the cube. It may be noted that only $\frac{1}{2}$ of each face sphere lies within the unit cell and there are six such faces.

The total contribution of 8 corners is $\left(\frac{1}{8}\times 8\right)$ = 1, while that of 6 face centred atoms is $\left(\frac{1}{2}\times 6\right)$ = 3 in the unit cell. Hence total number of atoms per unit cell is 1 + 3 = 4 atoms.

(c) Packing efficiency:

$$\text{P.E.} = \frac{z\times\frac{4}{3}\pi r^3}{V} = \frac{4\times\frac{4}{3}\pi\times\left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\% \quad [\because z = 4, r = \frac{a}{2\sqrt{2}}, V = a^3]$$

i.e. In FCC, 74% of total volume is occupied by atoms.

% void space = 26

SUMMARY TABLE

Unit cell	No. of atoms per unit cell	Relation between r & a	Co-ordination Number	Volume occupied by particles (%)
Simple cube	$8\times\frac{1}{8}=1$	$r=\frac{a}{2}$	6	$\frac{\pi}{6}\times 100 = 52.4$
Body centred cube (BCC)	$8\times\frac{1}{8}+1=2$	$r=\frac{a\sqrt{3}}{4}$	8	$\frac{\pi\sqrt{3}}{8}\times 100 = 68$
Face centred cube (FCC)	$8\times\frac{1}{8}+6\times\frac{1}{2}=4$	$r=\frac{a\sqrt{2}}{4}$	12	$\frac{\pi}{3\sqrt{2}}\times 100 = 74$

Illustration 5:

Assertion : A particle present at the corner of the face centred unit cell has 1/8th of its contribution to the unit cell.

Reason : In any space lattice, the corner of the unit cell is always shared by the eight unit cells.

(1) A (2) B (3) C (4) D

Ans (3)

Illustration 6:

In a face centred cubic arrangement of A and B atoms A are present at the corners and B at the face centres. It atoms are missing from 2 corners in each unit cell, then, what is the simplest formula of the compound?

Solution:

No. of A atoms = $6\times\frac{1}{8}=\frac{3}{4}$, No. of B atoms = $6\times\frac{1}{2}$ = 3

Formula = $A_{3/4}B_3 = AB_4$

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Illustration 7:

An element has an FCC structure in which edge length is 200 pm. If 200 g of element has 24×10^{23} atom, then, find out the density of solid

Solution:

$$d = \frac{z \times m}{N \times a^3}$$

$$d = \frac{4 \times 200}{24 \times 10^{23} \times (200 \times 10^{-10})^3}$$

$$d = \frac{4 \times 200}{24 \times 8 \times 10^{-1}}$$

$$d = \frac{4 \times 2000}{24 \times 8} = 41.67 g/cm^3$$

Illustration 8:

An element M has an fcc structure (M_w=100). Calculate the number of unit cells present in 10g of sample of element M.

Solution:

No. of atoms

$$= \text{mole} \times N_A = \frac{10}{100} \times N_A$$

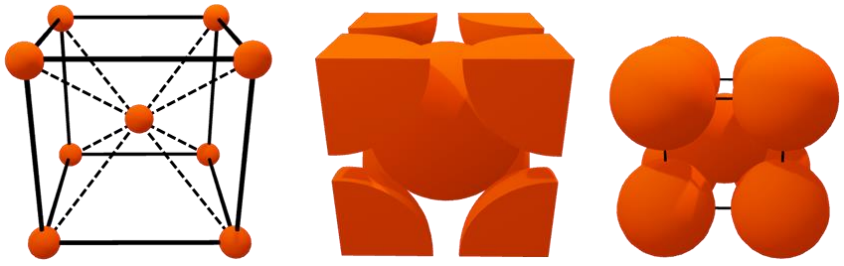
$$= \frac{N_A}{10}$$

$$\text{No. of unit lattice} = \frac{\text{No. of atoms}}{4} = \frac{N_A}{40}$$

(C) Body Centred Cubic Unit Cell (BCC)

A unit cell having lattice point at the body centre in addition to the lattice point at every corner is called as body centered unit cell.

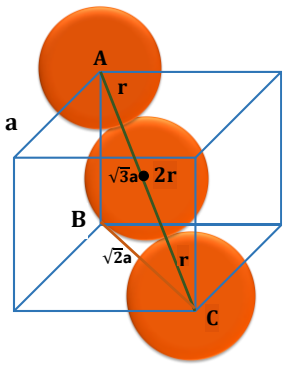
Here the central atom is surrounded by eight equidistant atoms and hence the co-ordination number is eight. The nearest distance between two atoms will be $\frac{a\sqrt{3}}{2}$



(a) Relationship between edge length 'a' and atomic radius 'r'

In BCC, along cube diagonal all atoms touch each other and the length of cube diagonal is $\sqrt{3}a$.

So, $\sqrt{3}a = 4r$ i.e. $\boxed{r = \frac{\sqrt{3}a}{4}}$



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(b) Number of atoms present in unit cell (z):

$z = \left(\frac{1}{8}\times 8\right) + (1 \times 1) = 1 + 1 = 2$ atoms/unit cell

(Corner) (Body centre)

In this case one atom lies at the each corner of the cube.

Thus contribution of the 8 corners is $\left(\frac{1}{8}\times 8\right) = 1$, while that of the body centred is 1 in the unit cell. Hence total number of atoms per unit cell is 1 + 1 = 2 atoms

(c) Packing efficiency:

$$\text{P.E.} = \frac{z\times\frac{4}{3}\pi r^3}{V} = \frac{2\times\frac{4}{3}\times\pi\left(\frac{\sqrt{3}a}{4}\right)^3}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68 \qquad [\because z = 2, r = \frac{\sqrt{3}a}{4}, V = a^3]$$

In B.C.C. , 68% of total volume is occupied by atoms.

% void space = 32

Illustration 9:

If the radius of an atom of an element is 75 pm and if the lattice is body-centred cubic then, the edge of the unit cell will be

(1) 32.475 pm (2) 173.2 pm (3) 37.5 pm (4) 212.1 pm

Solution:

$4r = a\sqrt{3}$

$a = \frac{4r}{\sqrt{3}} = \frac{4}{\sqrt{3}}(75)$

a = 173.2 pm

Illustration 10:

Na element crystalises in bcc structures. If the edge length is 300 pm, then, calculate the density of the solid.

Solution:

$$d = \frac{z\times M}{N_A\times a^3} = \frac{2\times 23}{6\times 10^{23}\times(300\times 10^{-10})^3}$$

$$= \frac{2\times 23}{6\times 27\times 10^{-1}}$$

$$= \frac{2\times 23\times 10}{6\times 27} = 2.8\,g/cm^3$$

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BEGINNER'S BOX-1

1. Aluminium (Molecular weight = 27) crystallises in a cubic unit cell with edge length a = 100 pm, with density, d = 180 g/cm^3, then type of unit cell is
(1) SC (2) BCC (3) FCC (4) HCP

2. An element has BCC unit cell with edge length 10Å. If density of element is 0.2 g/cm^3, then its molar mass is :-
(1) 240 (2) 60 (3) 35 (4) 280

3. In a tetragonal crystal :-
(1) a = b =c, $\alpha = \beta = 90° \neq \gamma$ (2) $\alpha = \beta = \gamma = 90°$, a = b ≠ c
(3) $\alpha = \beta = \gamma = 90°$, a ≠ b ≠ c (4) $\alpha = \beta = 90°$, γ=120°, a = b ≠ c

4. Edge length of a cube is 400 pm, its body diagonal would be ;-
(1) 500 pm (2) 600 pm (3) 566 pm (4) 693 pm

5. A metal crystallises into two cubic lattices fcc and bcc whose unit cell edge lengths are 3.5 and 3.0 Å respectively, the ratio of densities of fcc and bcc is :-
(1) 1.26 (2) 1.75 (3) 2.10 (4) 1.90

Close Packing of Identical Solid Spheres

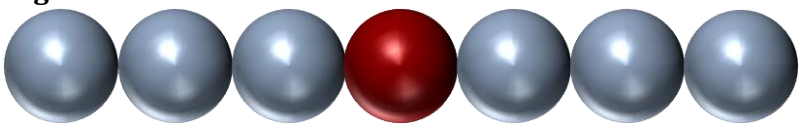
The solids which have non-directional bonding, their structures are determined on the basis of geometrical consideration. For such solids, it is found that the lowest energy structure is that in which each particle is surrounded by the greatest possible number of neighbours. In order to understand the structure of such solids, let us consider the particles as hard sphere of equal size in three directions. Although there are many ways to arrange the hard spheres but the one in which maximum available space is occupied will be economical which is known as closed packing, now we describe the different arrangements of spherical particles of equal size.

When the spheres are packed in a plane it gives two types of packing.

Types of Packing:

(A) Single line arrangement

(1) Close packing of atoms in one dimension

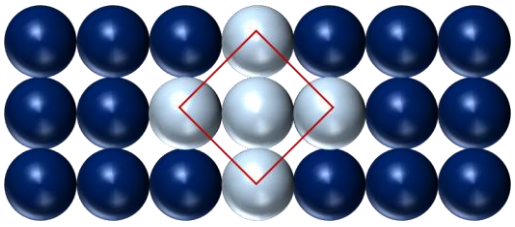


coordination number = 2

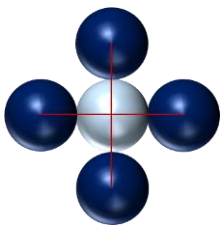
(B) Single layer arrangement

(2) Close packing of atoms in two dimensions: When the spheres are placed in a plane, it gives two type of packing.

(a) Square close packing: The centres of the spheres lie one below another. This type of arrangement is called square packing. In such packing one sphere touches four other spheres. In this case 52.4% of the volume is occupied. The remaining 47.6% of the volume is empty and is called void volume.



Square Packing



Z = 1, a = 2r, C.N. = 4, P.E. = 52.4%

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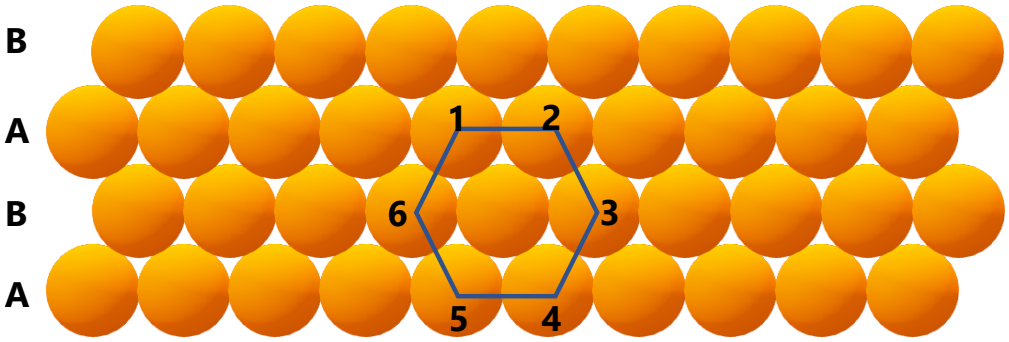
(b) Hexagonal close packing :- Another type of arrangement of atoms is shown below. This type of packing is called hexagonal packing. In such packing one sphere touches six other spheres. In this case 60.4% of the volume is occupied. The remaining 39.6% of the volume is empty and is called void volume. Therefore this type of packing is more compact than the square packing.

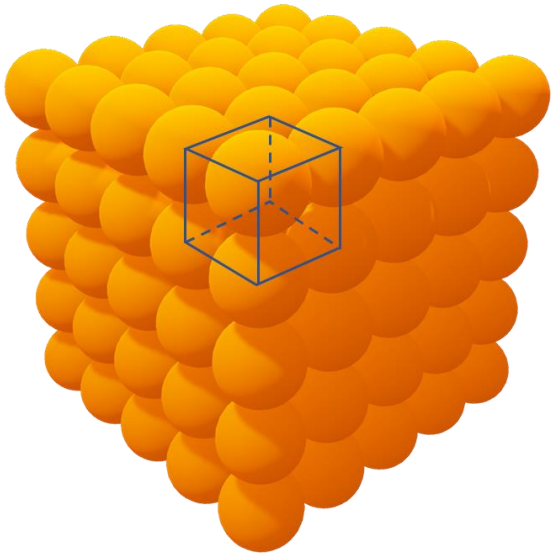


Hexagonal Packing, Z = 3, C.N. = 6, P.E. = 60.4%

(C) Multi layer arrangement:

(3) Close packing of atoms in three dimensions

(a) Simple cubic close packing



(Three dimensional close packing from two dimensional closed packed layers) When first square arrangement of layer A is exactly placed above occupies 2nd square arrangement of layer A and so on. So this type of arrangement is known as **AAA..... arrangement** and its unit cell is simple cubic unit cell.

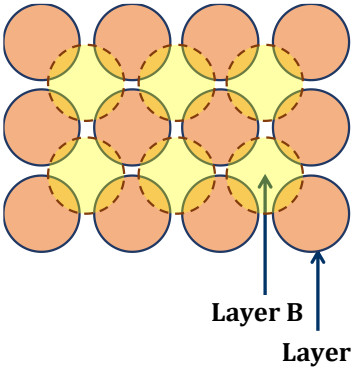
Simple cubic lattice formed by

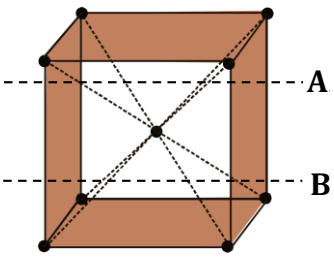
A A A .... Arrangement (type of packing)

Z = 1, C.N. = 6, P.E. = 52.4%.

It is not compact close packing.

(b) Body centred cubic close packing:

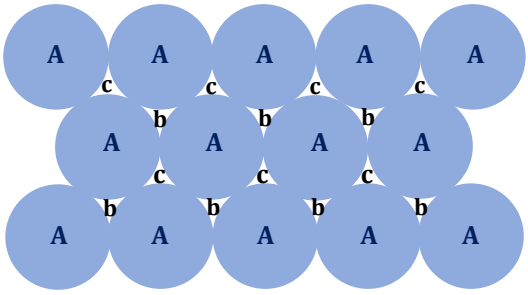




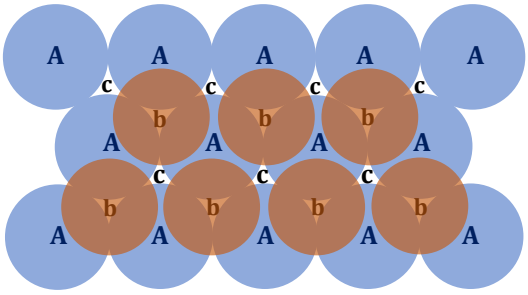
Body centred cubic lattice formed by ABAB ..... arrangement (type of packing)

Z = 2, C.N. = 8, P.E. = 68%. It is not compact close packing.

(c) Cubic close packing and hexagonal close packing: (Three dimensional close packing from two dimensional hexagonal close packed layers)

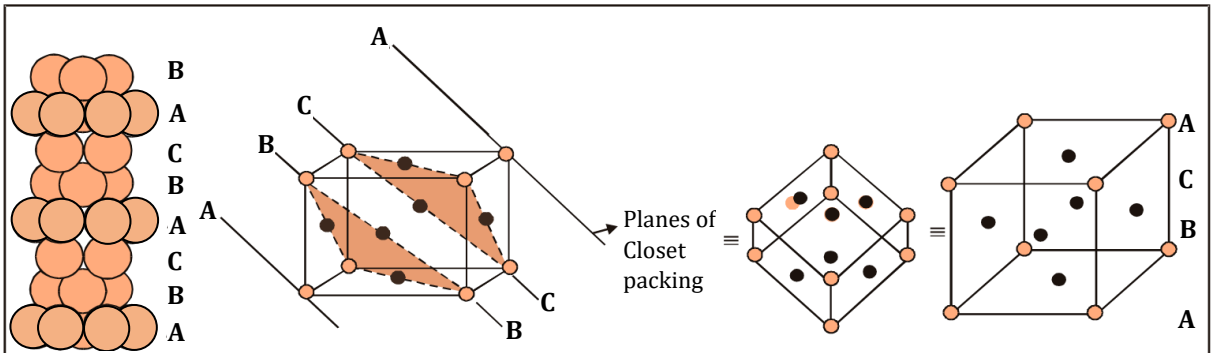


Layer A → [b, c] type voids

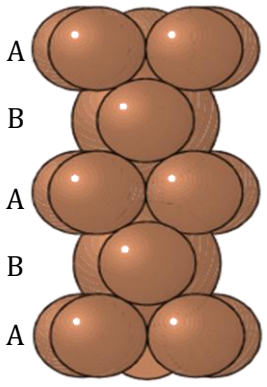


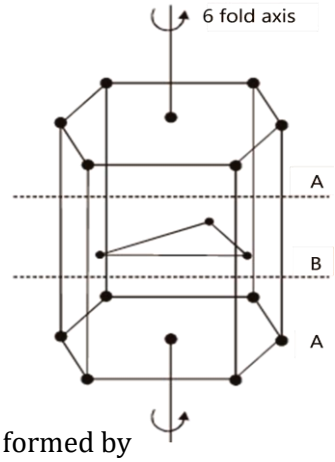
Layer B → [c, a] type voids

Cubic close packing

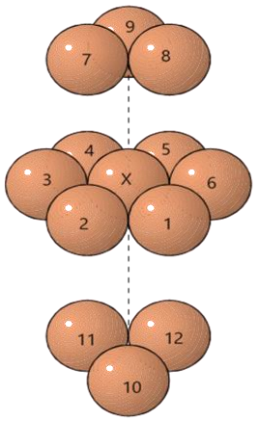


Cubic close packing lattice formed by ABCABCA …….. Arrangement (type of packing Z=4, C.N.=12, P.E. = 74%. CCP is compact close packing.





Hexagonal close packing lattice is formed by arrangement (type of packing). HCP is compact close packing.



Coordination number of hcp and ccp structure

Hexagonal close packing:

Number of particles in hexagonal unit cell (z) = $12\times\frac{1}{6}+2\times\frac{1}{2}+3\times1=6$

C.N. = 12, P.E. = 74%, type of packing ABAB.....

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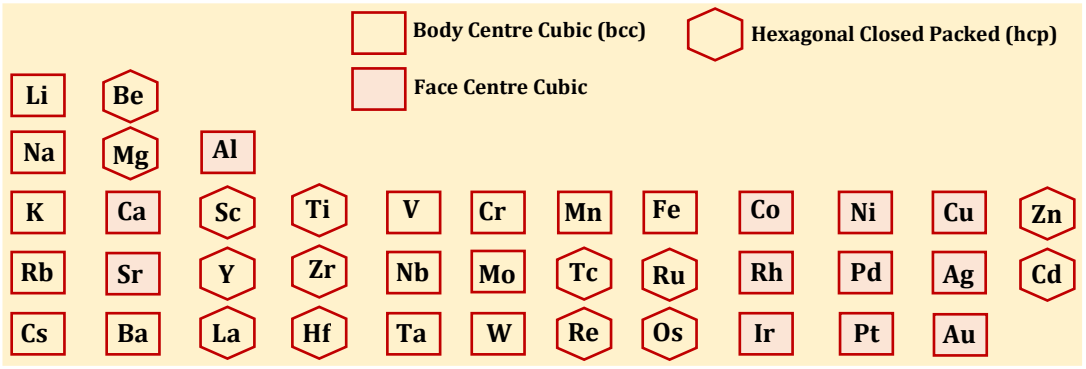
Golden Key Points

- Some examples of metals with their lattice types and coordination number are given in the following table.



Multiplayer Close Packing

Contents	SCC	BCC	CCP/FCC	HCP
Type of packing	AAAA.... packing	ABAB.... packing	ABCABC..... close packing	ABAB..... close packing
No. of atoms	1	2	4	6
Co-ordination no.	6	8	12	12
Packing efficiency	52.4%	68%	74%	74%
Examples	Po	IA, Ba V & Cr group Fe, Me	Ca, Sr, Al Co group, Ni group, Copper group, all inert gases except He	Remaining d-block elements Be & Mg

- In close packing, number of particles = N, number of OHV = N, Number of THV = 2N

Illustration 11:

The arrangement of the first two layers, one above the other, in HCP and CCP arrangements is

(1) Exactly same in both cases
(2) Partly same and partly different
(3) Different from eath other
(4) Nothing definite

Ans. (1)

Illustration 12:

"There is no difference in the arrangement of atoms in CCP and HCP structure" Do you agree with this statement? Explain why.

Solution:

Statement is incorrect

CCP ABCABCABC ....

HCP ABABAB .....

Interstices or Voids or Holes in Crystals

It has been seen that even through the particles are closely packed in the crystals but still there is some empty space left in between the spheres. This is known as interstices (or interstitial site or hole or empty space or voids). In three dimensional close packing (CCP & HCP) the interstices are of two types: (i) tetrahedral interstices and (ii) octahedral interstices.

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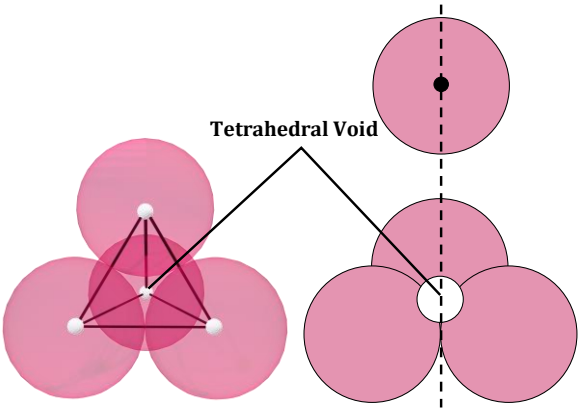
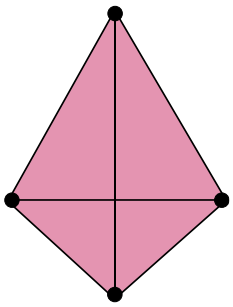
(A) Tetrahedral Interstices

We have seen that in hexagonal close packing (HCP) and cubic close packing (CCP) each sphere of second layer touches with the three spheres of first layer. Thus, they leave a small space in between which is known as **tetrahedral site or interstices** or the vacant space between 4 touching spheres is known as tetrahedral void. Since a sphere touches three spheres in the below layer and three spheres in the above layer hence there are two tetrahedral sites associated with one sphere.



A Tetrahedral interstices



Tetrahedron Geometry

It may by noted that a tetrahedral site does not mean that the site is tetrahedral in geometry but it means that this site is surrounded by four spheres and by joining the centres of these four spheres forms a regular tetrahedron.

In FCC, one corner and its three face centres form a tetrahedral void

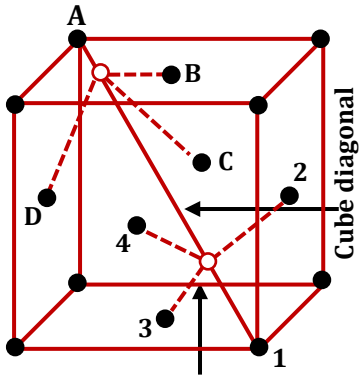
In FCC, two tetrahedral voids are obtained along one cube diagonal.

So in FCC, 8 tetrahedral voids are present.

In FCC, total number of atoms = 4

In FCC, total number of tetrahedral voids = 8

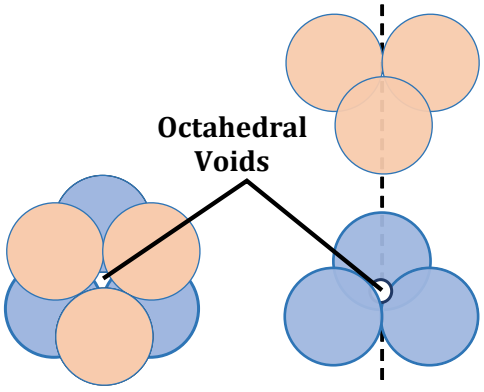
So, we can say that, in 3D close packing 2 tetrahedral voids are attached with one atom.



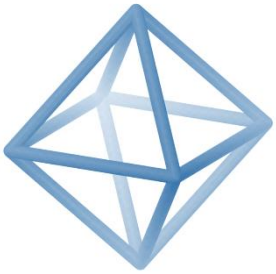
Tetrahedral void

(B) Octahedral Interstices

Hexagonal close packing (hcp) and cubic close packing (ccp) also form another type of interstices which is called as an octahedral site. The vacant space between 6 touching spheres is called as an octahedral void.



Octahedral interstices



Octahedral geometry

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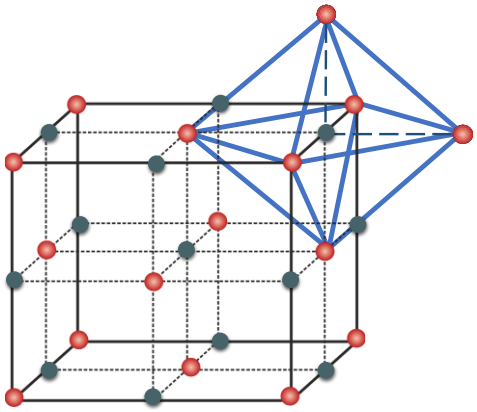
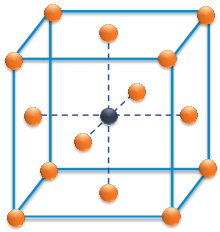
In the figure, two layers of close packed spheres are shown. The spheres of first layer are shown in blue while that of second layer in brown. Two triangles are drawn by joining the centres of three touching spheres of both the layers.

In fcc, 6 face centres form a octahedral void. On super imposing these triangles on one another one octahedral site is created. It may be noted that an octahedral site does not mean that the hole is octahedral in shape but it means that this site is surrounded by six nearest neighbour lattice points arranged octahedrally.



Octahedral Void (at the edge)
($1/4^{th}$ part of octahedral Void is obtained at each edge)



Octahedral Void
(at the body center)

In FCC, total number of octahedral voids

$= (1 \times 1) \quad + \quad (12 \times \frac{1}{4}) \quad = 1 + 3 = 4$

(Cube centre) (edge centre)

In FCC, number of atoms = 4 and number of octahedral voids = 4 : number of tetrahedral voids = 8

So we can say that, in 3D close packing one octahedral void is attached with one atom.

Illustration 13:

The number of octahedral sites in a cubical close packed array of N spheres is

(1) N/2 (2) 2N (3) N (4) 4N

Ans. (3)

Illustration 14:

Atom A is present at every element of FCC, atom B is present at every Octahedral void, atom C is present at 25% of the Tetrahedral voids. Find out the possible molecular formula of the compound ?

Solution:

Atom A is present at every element of FCC = 4 atoms of A

Atom B is present at every octahedral void = 4 atoms of B

Atom C is present at 25% of tetrahedral voids = $8 \times \frac{25}{100}$ = 2 atoms of C

So, the possible molecular formula is $A_4B_4C_2 = A_2B_2C$.

Study of Ionic Crystals

Limiting Radius Ratio

An ionic crystal contains a large number of cations and anions. Generally cations are smaller in size than that of anions. The cations are surrounded by anions and they touch each other. These ions are arranged in space in such a way so as to produce the maximum stability.

So the limiting radius ratio tells about:

(i) Stability of ionic crystal

(ii) Coordination number of smaller ion placed in the void.

(iii) Geometry of void

(a) Triangular : All anions touch each other and co-ordination number of cation is 3

$\cos\theta = \frac{R}{R+r}$

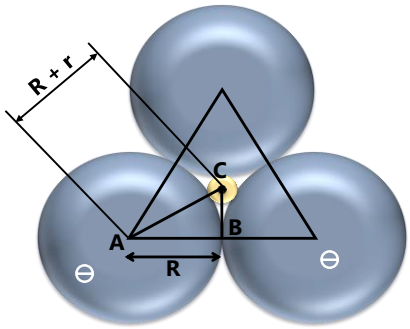
$\cos 30 = \frac{R}{r+R}$

$\sqrt{3}\,R + \sqrt{3r} = 2R$

$\sqrt{3r} = (2 - \sqrt{3})R$

$\frac{r}{R} = \frac{2-\sqrt{3}}{\sqrt{3}} = \frac{2-1.73}{1.73} = \frac{0.27}{1.73} = 0.155$

L.R.R. = $0.155 = \frac{r}{R} < 1$



(b) Tetrahedral void : All anions touch each other and co-ordination number of cation is 4.

Face diagonal AC = $\sqrt{2}a = 2R$

$R = \frac{a}{\sqrt{2}}$ **or** $a = \sqrt{2}R$

Triangle ACD - $AD^2 = AC^2 + CD^2$

$AD^2 = (\sqrt{2}a)^2 + (a)^2 = 2a^2 + a^2 = 3a^2$

$AD = \sqrt{3}\,a$

According to cube diagonal AD

$\because \frac{\sqrt{3}}{2}a = r + R$

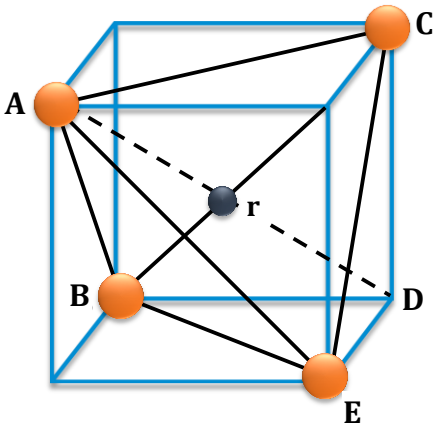
$\therefore \sqrt{3}a = 2r + 2R = AD$

Put the value of a = $\sqrt{2}R$

$\sqrt{3} \times \sqrt{2}R = 2r + 2R$

$\frac{\sqrt{3}\times\sqrt{2}R}{2R} = \frac{2r+2R}{2R}$ or $\frac{\sqrt{3}}{\sqrt{2}} = \frac{r}{R} + 1$

$\frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}} - 1 = \frac{\sqrt{3}-\sqrt{2}}{\sqrt{2}} = \frac{1.73-1.414}{1.414} = 0.225$



(c) Octahedral void: All the anions are touch each other and co-ordination number of cation is 6.

In ΔABC

$AC^2 = AB^2 + BC^2$

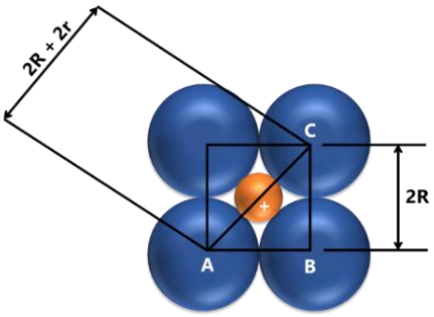
$(2R + 2r)^2 = (2R)^2 + (2R)^2$

$(2R + 2r) = \sqrt{8R^2}$

$2R + 2r = 2\sqrt{2}R$

$2R(\sqrt{2} - 1) = 2r$

$\frac{r}{R} = \sqrt{2} - 1 = 0.414$



(d) Cubic void: All the anions touch each other and co-ordination number of cation is 8.

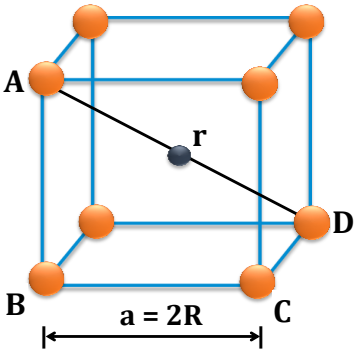
According to cube diagonal

$AD = \sqrt{3}\,a = 2r + 2R$ $(a = 2R = BC)$

$\sqrt{3} \times 2R = 2R + 2R$

Dividing by 2R on both sides.

$\sqrt{3} = \frac{r}{R} + 1 \Rightarrow \frac{r}{R} = \sqrt{3} - 1 = 1.732 - 1 = 0.732$



Golden Key Points

- The preferred direction of the structure with increase in the radius ratio is as follows:
  Plane triangular $\xrightarrow{0.225}$ Tetrahedral $\xrightarrow{0.414}$ octahedral $\xrightarrow{0.732}$ Cubic

- **Limiting Radius Ratio for Various Types of Voids**

Limiting radius ratio = r/R	Coordination Number	Structural Arrangement (Types of voids)	Example
$0.155 \le r/R < 0.225$	3	Plane Triangular	Boron Oxide (B_2O_3)
$0.255 \le r/R < 0.414$	4	Tetrahedral	ZnS, SiO_2
$0.414 \le r/R < 0.732$	6	Octahedral	NaCl, MgO
$0.732 \le r/R < 1.000$	8	Cubic	CsCl

Illustration 15:

Two ions A^+ and B^- have radius 86 and 200 pm respectively in a closed packed crystal of compound AB. Find out the C.N. of cation.

Solution:

Radius ratio = $\frac{r_+}{r_-} = \frac{86}{200} = 0.43$ C.N. = 6

Illustration 16:

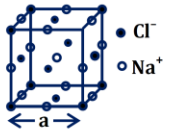
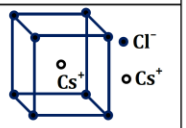
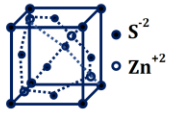
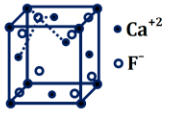
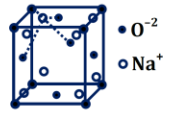
A solid crystal AB has NaCl type of a structure. If radius of anion is 200 pm, then, the radius of cation will be-

Solution:

Radius ratio = $\frac{r_+}{r_-} = 0.414$

$r_+ = 0.414 \times 200$ pm = 82.8 pm

SOME IONIC CRYSTALS

S. No.	Type of Crystal	Geometry	Co-ordination Number	No. of formula's per Unit Cell	Examples
1	NaCl (1 : 1) (Rock Salt Type)	C.C.P < Na^+→At every OHV Cl^-→Every element of C.C.P	6 : 6	$4Na^+ + 4Cl^-$ 4NaCl (4)	Halides of (Li, Na, K, Rb) Oxides and sulphides of a alkaline, earth metals (Except BeS) AgCl, AgBr, NH_4X 
2	CsCl Type (1 : 1)	B.C.C Type < Cs^+→At body centre (at cubic void) Cl^-→At every corner	8 : 8	$1Cs^+ + 1Cl^-$ 1CsCl (1)	Halides of 'Cs' TlCl, TlBr, CaS 
3	ZnS Type (1 : 1) (Zinc Blende Type) (Sphalerite)	C.C.P < Zn^{+2}→At 50% of T.H.V. or at alternate tetrahedral void S^{+2}→Every element of C.C.P.	4 : 4	$4Zn^{+2} + 4S^{-2}$ 4ZnS (4)	BeS, BeO, CaO, AgI, CuCl, CuBr, CuI 
4	CaF_2 Type (1 : 2) (Fluorite Type)	C.C.P < Ca^{+2}→Every element of C.C.P F^-→At every T.H.V	$4Ca^{+2}, 8F^-$ 8 : 4	$4Ca^{+2} + 8F^-$ $4CaF_2$ (4)	$BaCl_2$, BaF_2 $SrCl_2$, SrF_2, $CaCl_2$, CaF_2 
5	Na_2O Type (2 : 1) (Antifluorite)	C.C.P < Na^+→ At every T.H.V. O^{-2}→ Every element of C.C.P.	$8\ Na^+, 4O^{-2}$ 4 : 8	$8Na^+ + 4O^{-2}$ $4Na_2O$ (4)	Li_2O, Li_2S N_2O, Na_2S K_2O, K_2S 
6	ZnS Type (1 : 1) (Wurtzite) Another geometry of ZnS	H.C.P < Zn^{2+}→ 50% of T.H.V. or (at alternate T.H.V. S^{-2}→ Every element of H.C.P.	4 : 4	$6Zn^{+2} + 6S^{-2}$ 6ZnS (6)	Same as sphalerite

NaCl TYPE

For NaCl :

Distance between two nearest ions ($r^+ + r^-$):

$2r^+ + 2r^- = a$

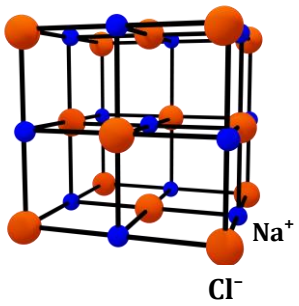
i.e. $\boxed{r^+ + r^- = \frac{a}{2}}$

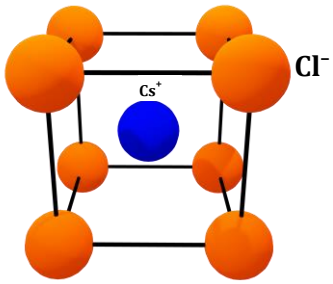
CsCl TYPE

For CsCl :

Distance between two nearest ions ($r^+ + r^-$):

$2r^+ + 2r^- = \sqrt{3}a$ i.e. $\boxed{r^+ + r^- = \frac{\sqrt{3}}{2}a}$





In both the structures cation and anion can exchange their position.

Structure of diamond: Solids which follow structure of diamond is known as diamond cubic. Diamond has CCP structure where carbon atoms are present at corners and face centre with four more atom present at alternate tetrahedral voids or 50% THV, so, total number of effective atoms

$$z = \left(8\times\frac{1}{8}+6\times\frac{1}{2}\right)+(4\times2)\times\frac{1}{2}=8$$

The carbon atoms present in THV touches its four surrounding atoms so coordination number is equal to four.

$$2r = \frac{\sqrt{3}}{4}a\,;\ a = \frac{8r}{\sqrt{3}}\,;\ PE = \frac{8\times\frac{4\pi}{3}r^3}{\left(\frac{8r}{\sqrt{3}}\right)^3} = 0.34\,;\ \text{So \% PE} = 34$$

Illustration 17:

Each unit cell of NaCl consists of 14 Cl^- ions and

(1) 13 Na^+ (2) 14 Na^+ (3) 6 Na^+ (4) All are wrong

Ans. (1)

Illustration 18:

A solid A^+B^- has NaCl type close packed structure. If the anion has a radius of 250 pm, what should be the ideal radius for the cation? Can a cation C^+ having a radius of 180 pm be slipped into the tetrahedral site of the crystal A^+B^- ? Give reason for your answer.

Solution:

In Na^+Cl^- crystal each Na^+ ion is surrounded by 6 Cl^+ ions and vice versa. Thus Na^+ ion is placed in octahedral hole.

The limiting radius ratio for octahedral site = 0.414 or = $\frac{r_{A^+}}{r_{B^-}} = \frac{r}{R} = 0.414$

Given that radius of anion (B^-) R = 250 pm

$\Rightarrow$ radius of cation (A^+) r = 0.414 R = 0.414 × 250 pm = 103.5 pm

Thus ideal radius for cation (A^+) is r = 103.5 pm.

We know that (r/R) for tetrahedral hole is 0.225.

$\therefore\ \frac{r}{R} = 0.225$: So, r = 56.25 pm

Thus the ideal radius for cation is 56.25 pm for a tetrahedral hole. But the radius of C^+ given is 180 pm which is much larger than the ideal radius of 56.25 pm. Therefore, we can not slip cation C^+ into the tetrahedral site.

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Illustration 19:

In the calcium fluoride structure, the co-ordination number of the cations and anions are respectively

(1) 6, 6 (2) 8, 4 (3) 4, 4 (4) 4, 8

Solution:

The Ca^{2+} ions are arranged in (ccp) arrangement, i.e. Ca^{2+} ions are present at all corners and at the centre of each face of the cube. The fluoride ions occupy all the tetrahedral sites. This is 8 : 4 arrangement i.e., each Ca^{2+} ion is surrounded by $8F^-$ ions and each F^- ion is surrounded by four Ca^{2+} ions.

Illustration 20:

In A^+B^- ionic compound, radii of A^+ and B^- ions are 180 pm and 187 pm respectively. The crystal structure of this compound will be

(1) NaCl type (2) CsCl type (3) ZnS type (4) Similar to diamond

Solution:

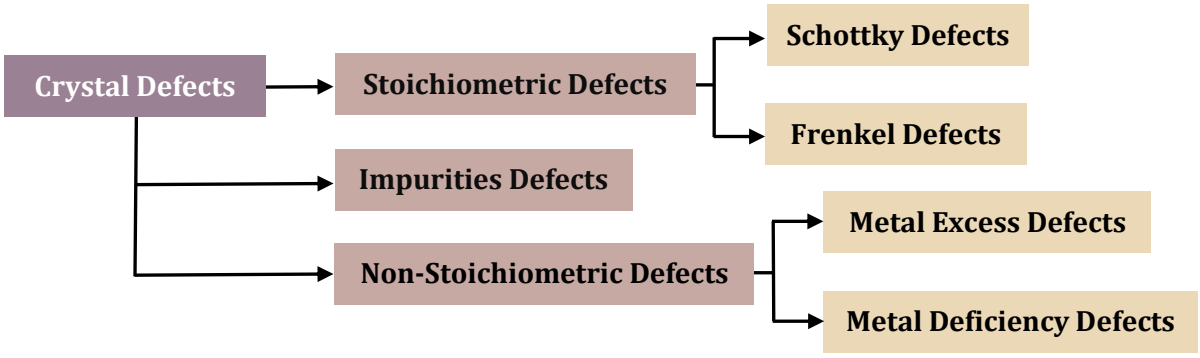
$$\frac{r_+}{r_-}=\frac{180}{187}=0.962$$

which lies in the range of 0.732 – 1.000, hence co-ordination number = 8 i.e. the structure is CsCl type.

Defects or Imperfections in Solids

Ideal crystal: The crystal in which all the lattice points are occupied by the component particles or groups of particles is called an ideal crystal. Ideal crystals are grown up at absolute kelvin temperature (zero K).

Solid state is characterised by vibratory motion about the mean position of constituent particles. At absolute zero, all the types of motions cease, and therefore crystals tend to have a perfectly ordered arrangement. As the temperature increases, molecular motions (vibratory amplitudes) increase and therefore the ions may lose their usual sites and either get missed or occupy interstitial positions in the crystal, ie., deviations from ordered arrangement take place. Any deviation from the perfectly ordered arrangement gives rise to a defect or imperfection in the crystal. Defect in crystals are produced either due to thermal effects or by adding certain impurities in the pure crystals (doping). Defects in crystals may be discussed as



(A) Stoichiometric Defects

Stoichiometric compounds are those compounds in which the number of positive and negative ions are exactly in the ratio as shown by their chemical formulae. Two types of defects are observed in these compounds.

(a) Schottky defect (b) Frenkel defect

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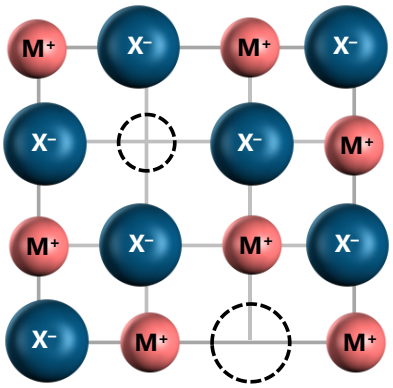
(a) Schottky defect: This type of defect is produced when equal number of cations and anions are missing from their respective positions leaving behind a pair of holes. The crystal as a whole remains neutral because the number of missing positive ions (cations) and negative ions (anions) are same.

- It is a kind of a vacancy defect.
- Schottky defect appears generally in ionic compounds in which radius ratio [r^+/r^-] is not far below unity. For this defect, the cations and anions should not differ much in size.
- For schottky defect, co-ordination numbers of the ions should be high. Examples of ionic solids showing this defect are NaCl, CsCl, KCl, AgBr etc.



Schottky Defect

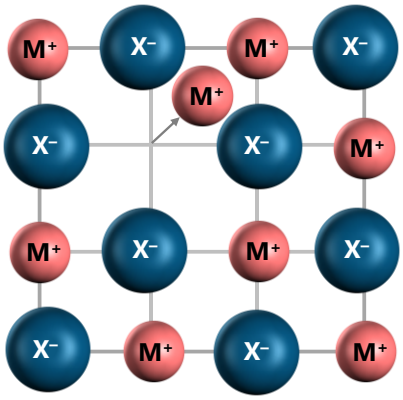
Consequences of schottky defect:

- Density of the crystal decreases
- The crystal begins to conduct electricity to small extent by ionic mechanism.
- The presence of too many 'voids' lowers the lattice energy or the stability of the crystal.

(b) Frenkel defect: This type of defect is created when an ion leaves its appropriate site in the lattice and occupies an interstitial site. A hole or vacancy is thus produced in the lattice.

The electroneutrality of the crystal is maintained since the number of positive and negative ions are same. Since positive ions are smaller in size, they usually leave their positions in the lattice and occupy interstitial positions. It is also called as the dislocation defect.

Frenkel defect is exhibited in ionic compounds in which the radius ratio [r^+/r^-] is low. The cations and anions differ much in their sizes and the ions have low co-ordination numbers. Examples are ZnS, AgBr, AgI, AgCl etc.



Frenkel Defect

Consequences of Frenkel defect:

- It is a kind of a dislocation defect.
- The closeness of like charges tend to increase the dielectric constant of the crystal.
- The crystal showing Frenkel defect conducts electricity to a small extent by ionic mechanism.
- The density of the crystal remains same.

(B) Impurity Defect

If molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+}. Each Sr^{2+} replaces two Na^+ Ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of Sr^{2+} ions. Another similar example is the solid solution of $CdCl_2$ and AgCl.

(C) Non-stoichiometric Defects

These type of defects are observed in the compounds of transition elements. These defects arise either due to the presence of excess metal ions or excess non-metal ions.

(a) Metal excess defect due to anion vacancies: A compound may have excess metal ion if an anion (negative ion) is absent from its appropriate lattice site creating a 'void' which is occupied by an electron. Ionic crystal which are likely to posses schottky defect, may also develop this type of metal excess defect. When alkali metal halides are heated in a atmosphere of vapours of the alkali metal, anion vacancies are created. The anions (halide ions) diffuse to the surface of the crystal from their appropriate lattice sites to combine with the newly generated metal cations. The electron lost by the metal atom diffuse through the crystal and occupy vacant anionic sites and are called as F-centres. The main consequence of metal excess defect is the development of colour in the crystal. For example, when NaCl crystal is heated in an atmosphere of Na vapours, it becomes yellow. Similarly, KCI crystal when heated in an atmosphere of potassium vapours, it appears violet.

(b) Metal excess defect due to interstitial cations: This type of defect is shown by crystals which are likely to exhibit Frenkel defect. An excess positive ion is located in the interstitial site. To maintain electrical neutrality, an electron is present in the intrestitial site. An example showing this type of defect is ZnO. When ZnO is heated, it loses oxygen $ZnO \xrightarrow{\text{On heating}} Zn^{2+} + \frac{1}{2}O_2$ gas. The excess Zn^{2+} ions are accommodated in the interstitial sites, the, electrons are enclosed in the neighbouring interstitials. The yellow colour of ZnO when hot is due to these trapped electrons. These electrons also explain electrical conductivity of the ZnO crystal.

(c) Metal Deficiency Defect

There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. A typical example of this type is FeO which is mostly found with a composition of $Fe_{0.95}O$. It may actually range from $Fe_{0.93}O$ to $Fe_{0.96}O$. In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+} ions.

★ Golden Key Points ★

- On increasing temperature coordination number decreases.
- On increasing pressure coordination number increases.
- If in a crystal complete lattice of ion along the line are disappear, such defect is called as the line defect.
- Schottky defects and Frenkel defects are point defects.

Illustration 21:

In the Schottky defect

(1) Cations are missing from the lattice sites and occupy the interstitial sites

(2) Equal number of cations and anions are missing

(3) Anions are missing and electrons are present in their place

(4) Equal number of extra cations and electrons are present in the interstitial sites

Ans. (2)

Illustration 22:

Schottky defect lowers the density of ionic crystals while Frenkel defect does not. Discuss.

Solution:

In Schottky defect, certain cations and anions are missing from the crystal lattice. Therefore, the density of the crystal decreases.However, in Frenkel defect the ions do not leave the lattice but they simply change their positions from lattice points to the interstitial spaces. As a result, the density of the crystal remains unchanged.

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BEGINNER'S BOX-2

1. The edge length of face centred cubic unit cell having rock salt structure is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is–
(1) 144 pm (2) 288 pm (3) 618 pm (4) 398 pm

2. In a solid 'AB' having the NaCl structure, 'A' atoms are arranged in CCP and B atoms are in OHV. If all the face-centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is–
(1) AB_2 (2) A_2B (3) A_4B_3 (4) A_3B_4

3. How many unit cells are present in a cube shaped ideal crystal of NaCl of mass 1.00 g ?
[Atomic mass : Na = 23, Cl = 35.5]
(1) 5.14×10^{21} (2) 1.28×10^{21} (3) 1.71×10^{21} (4) 2.57×10^{21}

4. A solid AB has the NaCl structure. If radius of the cation A^+ is 120 pm, the maximum value of the radius of the anion B^- is
(1) 290 pm (2) 350 pm (3) 250 pm (4) 400 pm

5. If the distance between Na^+ and Cl^- ions in sodium chloride crystal is x pm, then length of the edge of the unit cell is
(1) 2x pm (2) 4x pm (3) x/2 pm (4) x/4 pm

6. HCP crystal is made of A ions and B ions are arranged in 2/3rd of octahedral voids. The simplest formula of compound is
(1) A_4B_6 (2) A_6B_4 (3) A_2B_3 (4) A_3B_2

7. A FCC crystal of O^{-2} (oxide) ions has M^{+n} ions in 50% of octahedral voids, then the value of n is
(1) 2 (2) 3 (3) 4 (4) 1

8. If the edge length of a KCl unit cell is 488 pm, what is the length of KCl bond if it crystallises in the FCC structure ?
(1) 122 pm (2) 244 pm (3) 488 pm (4) 974 pm

9. In a solid lattice, the cation has left a lattice site and is located at interstitial position, the lattice defect is
(1) Interstitial defect (2) Vacancy defect (3) Frenkel defect (4) Schottky defect

BEGINNER'S BOX — ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5
	Ans.	3	2	2	4	1

BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7	8	9
	Ans.	1	4	4	1	1	4	3	2	3

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